

## **New Insights into Amino Acid Preservation in the Early Oceans using Modern Analytical Techniques**

Eric T. Parker<sup>1</sup>, Karen L. Brinton<sup>2</sup>, Aaron S. Burton<sup>3</sup>, Daniel P. Glavin<sup>4</sup>, Jason P. Dworkin<sup>4</sup>, and Jeffrey L. Bada<sup>5</sup>

<sup>1</sup>School of Chemistry and Biochemistry, Georgia Institute of Technology (erictparker@gatech.edu), <sup>2</sup>School of Mathematics, Science & Engineering, Southwestern College, <sup>3</sup>Astromaterials Research and Exploration Science Division, NASA Johnson Space Center, <sup>4</sup>Solar System Exploration Division, NASA Goddard Space Flight Center, <sup>5</sup>Geophysical Research Division Scripps Institution of Oceanography, University of California, San Diego.

Protein- and non-protein-amino acids likely occupied the oceans at the time of the origin and evolution of life. Primordial soup-, hydrothermal vent-, and meteoritic-processes likely contributed to this early chemical inventory. Prebiotic synthesis and carbonaceous meteorite studies suggest that non-protein amino acids were likely more abundant than their protein-counterparts. Amino acid preservation before abiotic and biotic destruction is key to biomarker availability in paleoenvironments and remains an important uncertainty.

To constrain primitive amino acid lifetimes, a 1992 archived seawater/beach sand mixture was spiked with D,L-alanine, D,L-valine (Val),  $\alpha$ -aminoisobutyric acid ( $\alpha$ -AIB), D,L-isovaline (Iva), and glycine (Gly). Analysis by high performance liquid chromatography with fluorescence detection (HPLC-FD) showed that only D-Val and non-protein amino acids were abundant after 2250 days.

The mixture was re-analyzed in 2012 using HPLC-FD and a triple quadrupole mass spectrometer (QQ-MS). The analytical results 20 years after the inception of the experiment were strikingly similar to those after 2250 days.

To confirm that viable microorganisms were still present, the mixture was re-spiked with Gly in 2012. Aliquots were collected immediately after spiking, and at 5- and 9-month intervals thereafter. Final HPLC-FD/QQ-MS analyses were performed in 2014.

The 2014 analyses revealed that only  $\alpha$ -AIB, D,L-Iva, and D-Val remained abundant. The disappearance of Gly indicated that microorganisms still lived in the mixture and were capable of consuming protein amino acids. These findings demonstrate that non-protein amino acids are minimally impacted by biological degradation and thus have very long lifetimes under these conditions.

Primitive non-protein amino acids from terrestrial synthesis, or meteorite in-fall, likely experienced greater preservation than protein amino acids in paleo-oceanic environments. Such robust molecules may have reached a steady state concentration dependent on ocean circulation through hydrothermal systems and synthetic input processes. We are presently trying to estimate this concentration.